Case No. GSC 11,304-1

THERMALLY CONDUCTIVE POLYMERS

Potting compositions for electrical components have long inflicted undesirable heat build-up upon the components they otherwise protect. It is accordingly an object to provide a material which effectively serves the normal functions of a potting composition and additionally provides sufficient heat transfer to avoid excessive heat build-up in the potted components.

The present invention provides such a material in the interpolymer of hydroquinone, phenol, and formaldehyde, prepared by conventional phenol-formaldehyde resin technology, and wherein hydroquinone replaces a portion of the phenol normally included. Figure 1 illustrates the effect of the inclusion of hydroquinone upon the thermal conductivity of such polymers. Figure 2 illustrates the comparative thermal behavior of a number of such polymers with a conventional phenol-formaldehyde polymer, designated A in the Figure.

The polymer is a novel contribution to the art and serves effectively as an electrical potting material while also providing a thermally conductive medium which substantially reduces heat build-up in potted components.

Inventors: Norman R. Byrd
Robert K. Jenkins
James L. Lister
McDonnell Douglas Corporation NAS5-10260

~~Evaluator: Mr. Charles A. Vest, NASA/GSFC~~

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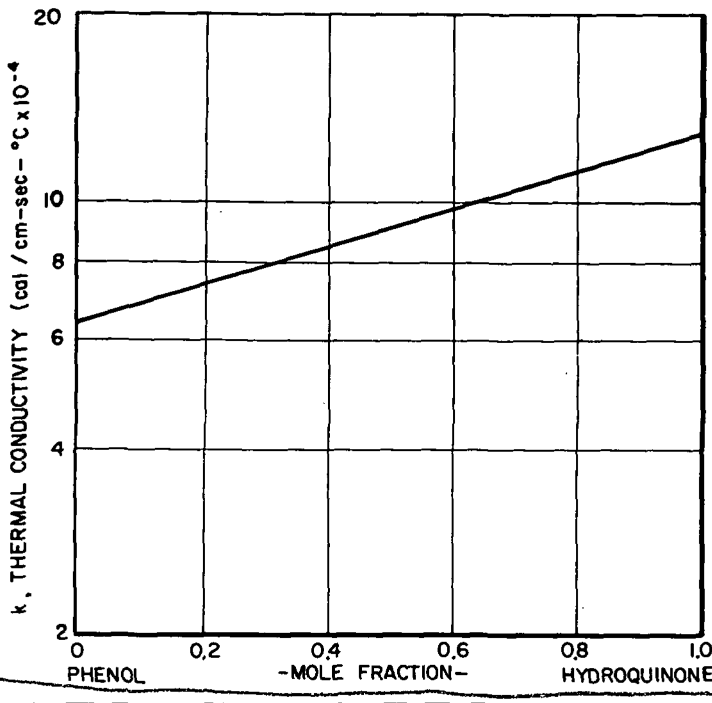
40%

FIG. 1



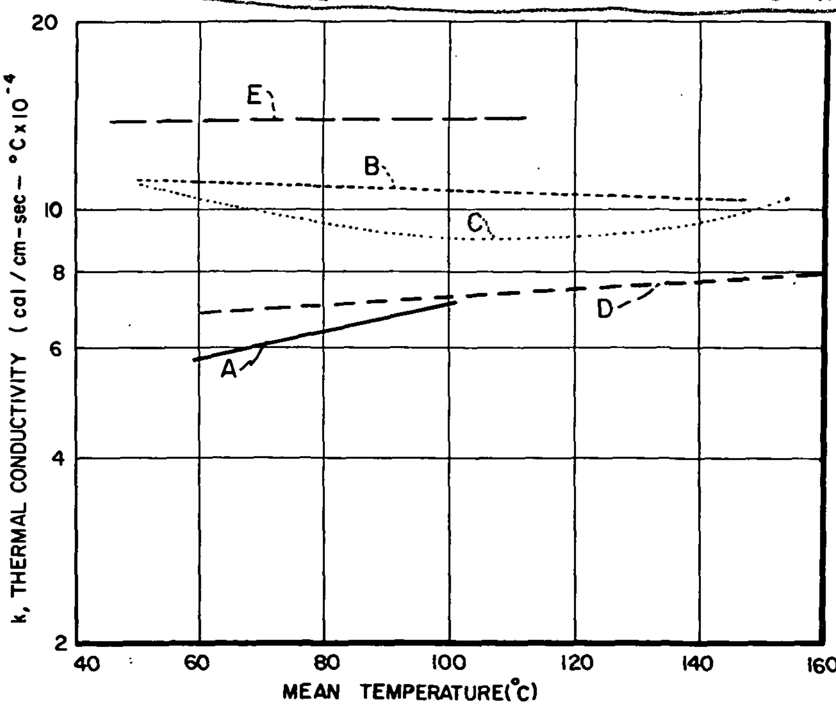


FIG. 2

INVENTORS
NORMAN R. BYRD
ROBERT K. JENKINS
JAMES L. LISTER

BY Robert F Kempf
ATTORNEY

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PRINT FIG. Figure 1

NOTICE

The invention disclosed in this document resulted from research in aeronautical and space activities performed under programs of the National Aeronautics and Space Administration. The invention is owned by NASA and is therefore available for licensing in accordance with the NASA Patent Licensing Regulation (14 Code of Federal Regulations 1245.200).

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APPLICATION FOR LETTERS PATENT

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT Norman R. Byrd, Robert K. Jenkins and James L. Lister

citizens of the United States of America,

and residents of Dana Point, California; Huntington Beach, California; and Anaheim, California, respectively,

have invented certain new and useful improvements in

THERMALLY CONDUCTIVE POLYMERS

of which the following is a specification:

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to thermally conductive polymers and, more particularly, to thermally conductive polymers and polymer compositions useful as coatings and potting materials for electronic components and the like and which serve to dissipate heat generated in such electronic components during operation. Still more particularly, the present invention relates to the preparation of polymers of phenol, formaldehyde, and hydroquinone, having a thermal conductivity of at least about 1.0×10^{-3} cal/cm-sec °C.

Prior Art

It has long been known to coat or pot electrical components with polymeric materials and compositions of a wide diversity of types to provide environmental protection, electrical insulation and shielding from mechanical, electrical and thermal shocks. Among the materials which have been employed for such purposes, the major classes have been, for example, epoxies and various modified epoxies, silicones, polybutadiene, butadiene-styrene copolymers, polyurethanes, phenolics, and

parylenes, i.e., poly-p-xylenes. Such potting materials have included fillers, plasticizers, and like additives where appropriate, as determined by the polymer characteristics and the parameters of usage.

Such systems have met with considerable success in meeting the requirements of operation for electronic components with regard to environmental factors and mechanical, thermal, and electrical shock, but because of the nature of the materials, have caused substantial problems and use limitations because of the heat build-up in and around components. The thermal conductivity of most of the electrically insulating polymers which provide adequate performance in other requisite characteristics is on the order of about 3×10^{-4} cal/cm-sec.-°C., and accordingly, operate effectively as a heat insulating material rather than as a conductor. As a consequence, the heat generated during operation of an electronic component rapidly accumulates rather than being dissipated, causing substantial perturbations in component performance, deterioration of heat sensitive elements, and, eventually, premature failure of the component. Accordingly, the desirability of a material, suitable in all respects as a coating and potting composition, and having increased and improved thermal conductivity, is readily apparent.

It is accordingly an object of the present invention to provide a synthetic polymer having increased thermal conductivity and more particularly to provide a polymer suitable for use as a coating and potting medium for electronic components which

has increased thermal conductivity. A further object of the present invention is to provide a polymer having a thermal conductivity greater than about 6 x 10^{-4} cal/cm.-sec.-°C., and preferably greater than about 1 x 10^{-3} cal/cm-sec.-°C.

SUMMARY OF THE INVENTION

The foregoing objects and still others which will become apparent from the following disclosure are attained by the present invention which comprises an interpolymer of phenol, formaldehyde, and hydroquinone. The polymer of the present invention can be conveniently described and understood as a phenol-formaldehyde polymer wherein a portion of the phenol component is replaced by hydroquinone. Thermal conductivity of the polymers of the present invention range from about 7 x 10^{-4} cal./cm.-sec.°C. up to as high as about 1.5 x 10^{-3} cal/cm.-sec.-°C.

DESCRIPTION OF THE DRAWINGS

In the drawings, Figure 1 is a graphical representation of thermal conductivity as a function of the mole ratios of phenol and hydroquinone in the polymers of the present invention at 80°C.

Figure 2 is a graphical representative of thermal conductivity as a function of mean temperature for a variety of the polymers of the present invention.

DETAILED DESCRIPTION

The polymers of the present invention are interpolymers of phenol, formaldehyde, and hydroquinone. Phenol-formaldehyde polymers are well known to the art, together with the various polymerization techniques and parameters of preparation, recovery, purification, and use. Such polymers are generally prepared by reacting the monomers in a basic aqueous medium at elevated temperatures, whereupon the polymer forms in solution. The polymer thus prepared can be cast directly from the aqueous medium into films, coatings, and the like, and cured to a relatively rigid, insoluble, infusible solid thermoset material by heating to moderate temperatures. Operations and the many variations thereupon are sufficiently well known to those of ordinary skill in the art so as to require no detailed explanation or instructions.

The polymers of the present invention differ from phenol-formaldehyde polymers only in the inclusion of hydroquinone as a partial replacement for the phenol monomer, and in the increased thermal conductivity which results. The preparation of the polymer, and properties other than thermal conductivity are not notably altered. Thus, for all intents and purposes, the polymers of the present invention can be formed, manipulated, and used as would be a conventional phenol-formaldehyde polymer.

As can be readily ascertained from Figure 1, the thermal conductivity of the polymers of the present invention steadily increases as the mole fraction of hydroquinone substituted for the phenol increases. However, as the amount of hydroquinone employed increases to above about 90% of the total of phenol and hydroquinone, the physical characteristics of the polymers are substantially altered, and the polymers are not so readily useful as potting compositions. Hence, it is preferable that the mole fraction of hydroquinone based on the total of hydroquinine and phenol be within the range of about 0.2 to 0.9, more preferably about 0.5 to 0.9. The relative amount of formaldehyde will vary from about 0.8 to 3.0 mole, preferably about 1.2 moles, per mole of combined phenol and hydroquinone, as is conventional practice in the preparation of phenol formaldehyde polymers.

It is hypothesized, although applicants have no wish to be bound thereby and expressly disclaim any limitation thereto, that the increase in thermal conductivity is attributable to the partial autoxidation of the hydroquinone component of the polymer to a quinoid structure similar to benzoquinone. Both the phenolic and hydroquinone moieties of the polymer are believed to form a charge-transfer coupling with the quinone structure. Inter- and intra-molecular charge transfer complexes probably result in the formation of pseudocrystalline regions of donor and acceptor molecules in a stacked structure. Such pseudocrystalline regions in an amorphous matrix give rise to enhanced phonon and electronic heat flow.

The preferred procedure for preparing the polymers of the present invention is illustrated in the following examples, and particularly in Example I, wherein the most preferred polymer of the present invention is exemplified, representing the best mode of practicing the invention.

Example 1

A one liter resin kettle equipped with a dropping funnel, reflux condenser, and stirrer was charged with one mole of phenol, one mole of hydroquinone, and 2.0 moles of formaldehyde in 100 milliliters of water. Four milliliters of a 50% NaOH aqueous solution was added and the mix was heated to reflux for three hours. A color change was observed, from amber to red and eventually to brown. The resulting solution was concentrated to 50% solids by evaporation and the polymer was then cast into a film, and cured according to the following cure schedule: 49°C - 3 hours; 71°C - 2 hours; and 110°C - 3 hours. The film was cooled slowly and measured for thermal conductivity. A value of 1.1×10^{-3} cal/cm-sec-°C. at a mean temperature of 80°C was observed. The excellent quality of the cast film made by this example, coupled with its high thermal conductivity and good electrical resistivity, makes the material suitable for use as a coating for electronic components.

Example II

Following the procedure of Example I, a series of polymers was formed having varying ratios of hydroquinone to phenol. The mole compositions were as follows in Table I.

The thermal conductivities are graphically illustrated in Figure 2.

Table I

Run	Phenol	Formaldehyde	Hydroquinone
A	1.0	1.5	-
B	1.0	2.0	1.0
C	1.0	3.0	2.0
D	2.0	3.0	1.0
E	-	1.0	1.0

Example III

Again following the procedure of Example I, a polymer was formed in mole ratios phenol, 1.0; hydroquinone, 1.0; and formaldehyde 2.4. The resultant polymer solution was concentrated to about 60% solids and utilized to spray coat a test circuit board. Films equivalent to those used as a coating on the circuit board were found to have a thermal conductivity of 10.6 x 10^{-4} cal/cm-sec-°C. at 60°C. and a resistivity at 1000 atm. of 3.9 x 10^9 ohm-cm.